

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 972 855 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
19.01.2000 Bulletin 2000/03

(51) Int Cl.7: C25B 1/00

(21) Application number: 99600008.9

(22) Date of filing: 01.07.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

• Marnellos, Georgos,
Foundation for Research and Technology-Hellas
57001 Thessaloniki (GR)

(30) Priority: 03.07.1998 GR 98100255

(71) Applicants:

- Foundation for Research and Technology
Hellas, Chemical Process,
Engineering Research Institute
57001 Thessaloniki (GR)
- Stoukides, Michael,
Foundation for Research and Technology-Hellas
57001 Thessaloniki (GR)

(72) Inventors:

- Stoukides, Michaelis,
Idrima Tehnologias ke erevmas
57001 Thessaloniki (GR)
- Marnellos, Georgos,
Idrima Tehnologias ke erevmas
57001 Thessaloniki (GR)

(74) Representative:

Koutifari, Ekaterini Georgiou et al
56 Omirou Street
108 72 Athens (GR)

(54) Method and apparatus for ammonia synthesis at atmospheric pressure

(57) Prototype reactor and method for the ammonia synthesis at atmospheric pressure. This invention relates to the ammonia production from its elements (N_2 and H_2) at atmospheric pressure. This was achieved in a solid state proton (H^+) conducting cell - reactor. Hydrogen was flowing over the anode (6) and was converted into protons that were transported through the solid electrolyte (4) and reached the cathode (5)(Pd) over which nitrogen was passing.

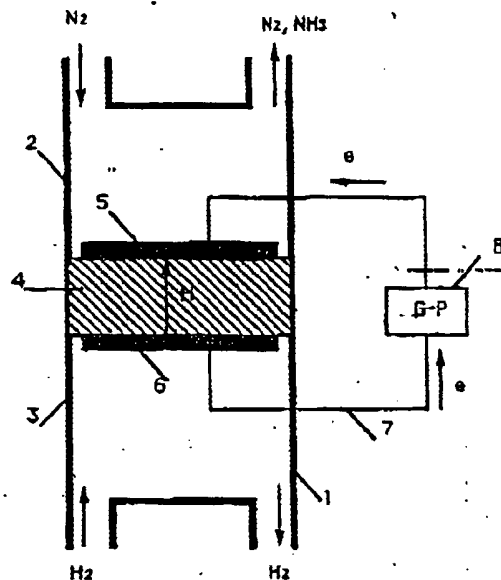


Figure 1

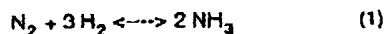
EP 0 972 855 A1

EP 0 972 855 A1

Description

[0001] The present invention relates to a method for synthesizing ammonia from its elements (H_2 and N_2) at atmospheric pressure. This was achieved in a prototype solid state proton (H^+) conducting cell-reactor.

[0002] The development of a successful process for ammonia synthesis from its elements:



is considered a landmark in heterogeneous catalysis. The Haber process which involves reaction of gaseous nitrogen and hydrogen on a Fe-based catalyst at high pressures (15 - 30 MPa), was developed at the beginning of the twentieth century after an extensive search for an active catalyst [1].

[0003] Even from early studies, it was realized that the conversion is limited by thermodynamics. The gas volume decreases with reaction. Hence, very high pressures have to be used in order to push equilibrium to the right according to the Le Chatelier principle.

[0004] The reaction is exothermic (109 kJ/mol at 500°C) and therefore conversion increases with decreasing temperature. In order to achieve however, industrially acceptable reaction rates, the reaction temperature must be high. The trade-off solution is to operate at temperatures in the range of 430 - 480°C, at which the equilibrium conversion is of the order of 10 - 15% [1].

[0005] The present method refers on an alternative route to ammonia synthesis at atmospheric pressure via the use of solid state proton (H^+) conductors by which the requirement for operation at high pressures is eliminated.

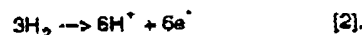
[0006] Solid electrolyte cells have been used so far in heterogeneous catalysis in order to a) study the mechanism of catalytic reactions [2, 3], b) electrochemically alter reaction rates [4, 5] and c) cogenerate electricity and useful chemicals [6]. The solid electrolytes used in most of the above applications were oxygen ion conductors.

[0007] In the last decade however, materials that exhibit protonic conductivity in the solid state have been introduced into catalysis research [7]. These H^+ conductors are particularly useful because they can operate at temperatures in which many industrial hydro- and dehydrogenation reactions take place. Furthermore, in contrast to oxidation reactions, a number of industrial hydrogenations (ammonia, methanol production) are equilibrium limited at the operating conditions.

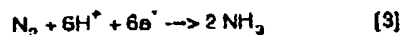
[0008] A model process using solid state proton conductors to obtain conversions higher than those predicted by the reaction equilibrium, has been proposed in the past [8]. It is possible to use two configurations. The double and the single chamber configuration.

[0009] In the double chamber configuration (Figure 1)

a vessel 1 has been divided into a hydrogenation reaction chamber 2 and into a chamber containing a hydrogen atmosphere 3, using a proton conducting solid electrolyte ($SrCe_{0.95}Yb_{0.05}O_3$) 4. Two porous polycrystalline palladium (Pd) films have been deposited inside and outside the solid electrolyte. The working electrode 5 was deposited in chamber 2 and served also as catalyst for the reaction of ammonia synthesis. The counter electrode 6 was deposited in the other side of the solid electrolyte, i.e. in chamber 3. These two electrodes are connected with Au wires 7 in a galvanostat - potentiostat 8. The cathode (chamber 2) was exposed to a gaseous stream containing nitrogen diluted in helium while the anode (chamber 3) was exposed to a hydrogen stream. The gaseous H_2 passing over the anode of the proton-conducting cell-reactor, will be converted to H^+ :



The protons (H^+) are transported through the solid electrolyte to the cathode where the half-cell reaction:

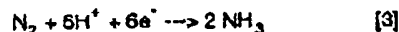


takes place. Thus, reaction [1] is again the overall reaction.

[0010] In the single chamber configuration (Figure 2) a reaction vessel 1 contains a proton conducting solid electrolyte ($SrCe_{0.95}Yb_{0.05}O_3$) 2. Two porous polycrystalline palladium (Pd) films have been deposited on the two sides of the solid electrolyte. The working electrode 3 was deposited in the one side of solid electrolyte and served also as catalyst for the reaction of ammonia synthesis. The counter electrode 4 was deposited in the other side of the solid electrolyte. These two electrodes are connected with Au wires 5 in a galvanostat - potentiostat 6. In the following a gaseous mixture containing nitrogen and hydrogen diluted in helium are fed to the reaction vessel 1. The gaseous H_2 passing over the anode of the proton-conducting cell-reactor, will be converted to H^+ :



The protons (H^+) are transported through the solid electrolyte to the cathode where the half-cell reaction:



takes place.

[0011] Specifically, this single chamber configuration is simpler than the double chamber configuration because of the fact that the complexity of the separation of the two chambers is avoided.

[0012] The ceramic material was a strontia-ceria-ytterbia (SCY) perovskite of the form: $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$. This perovskite is a solid with good mechanical strength and with high protonic conductivity [9]. The electrode preparation and characterization procedure has been described in detail elsewhere [10].

[0013] Figure 3 shows the dependence of the rate of NH_3 formation in a double chamber cell on $I/2F$, where I is the imposed current and F is Faraday's constant. Assuming that the SCY is solely a proton conductor, the ratio $I/2F$ is equal to the electrochemical molar flux of hydrogen through the solid electrolyte. The cell was kept at 570°C . A mixture of 1.8% N_2 in He was passing over the cathode at a volumetric flowrate of $8.3 \times 10^{-8} \text{ m}^3/\text{s}$ and atmospheric total pressure. A flow of $5.0 \times 10^{-7} \text{ m}^3/\text{s}$ of 100% H_2 at atmospheric pressure was maintained over the anode. At $I=0$, no products were formed. Upon imposing a current through the cell, NH_3 appeared at the cathode and after a transient period of 2-6 minutes, a steady state rate of NH_3 formation was established.

[0014] The data points in Figure 3 represent steady state rates. The two dotted lines of Figure 3 are based on thermodynamic calculations and are represented for comparison of the present results with those that would have been obtained in a conventional catalytic reactor (CCR) in which gaseous H_2 rather than electrochemical H^+ were used. Specifically, the curve denoted as CCR represents the maximum rate of NH_3 formation attained in a CCR that operates at 570°C and at atmospheric pressure and in which the same amounts of N_2 and H_2 as in the present experiments, are introduced. It can be seen that the NH_3 rates attained experimentally exceed the CCR rates by at least three orders of magnitude. Similarly, the curve denoted as PCCR (pressure in a conventional catalytic reactor) represents the total pressure at which a CCR should operate in order for the NH_3 conversion to be as high as that reported here.

[0015] Figure 4 shows the dependence of the rate of NH_3 formation in a single chamber cell on $I/2F$, where I is the imposed current and F is Faraday's constant. The cell was kept at 600°C . A gas mixture of N_2 (0.5%), H_2 (10%) and He was fed on the reaction vessel at a volumetric flowrate of $3.3 \times 10^{-7} \text{ m}^3/\text{s}$ and atmospheric total pressure. At $I=0$, no products were formed. Upon imposing a current through the cell, NH_3 appeared at the cathode and after a transient period of 2-6 minutes, a steady state rate of NH_3 formation were established.

[0016] The data points in Figure 4 represent steady state rates. The two dotted lines of Figure 4 are based on thermodynamic calculations and are presented for comparison of the present results with those that would have been obtained in a conventional catalytic reactor (CCR) in which gaseous H_2 rather than electrochemical H^+ were used. Specifically, the curve denoted as CCR represents the maximum rate of NH_3 formation attained in a CCR that operates at 600°C and at atmospheric pressure and in which the same amounts of N_2 and H_2 as in the present experiments, are introduced. It can be

seen that the NH_3 rates attained experimentally exceed the CCR rates by at least two orders of magnitude. Similarly, the curve denoted as PCCR (pressure in a conventional catalytic reactor) represents the total pressure at which a CCR should operate in order for the NH_3 conversion to be as high as that reported here.

1. C.N. Satterfield, *Heterogeneous Catalysis in Practice*, (McGraw-Hill, New York, 1980), pp. 301-308.
2. M. Stoukides, *Ind Eng. Chem. Res.*, 27, 1745 (1988).
3. C. G. Vayenas, M.M. Jaksic, S.I. Babalis and S. G. Neophytides, in *Modern Aspects in Electrochemistry*, J.O'M Bockris, B. E. Conway and W.R.E. White, Eds. (Plenum, New York, 1996) vol. 29, 57 (1996).
4. T. M. Gür and R. A. Huggins, *Science*, 219, 967 (1983).
5. Y. Jiang, I. V. Yentekakis and C.G. Vayenas, *Science*, 264, 1563 (1994).
6. C.G. Vayenas and R.D. Fart, *Science*, 208, 593 (1980).
7. H. Iwahara, *Sol. St. Tonics*, 86-88, 9 (1996).
8. E. Panagos, I. Voudouris and M. Stoukides, *Chem. Eng. Sci.*, 51, 3175 (1996).
9. H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Sol. St. Tonics*, 3/4, 359 (1981).
10. C. Athanasiou, G. Mamellos, P. Tsiakaras and M. Stoukides, *Tonics*, 2, 353 (1996).

Claims

1. The process for synthesizing ammonia at atmospheric pressure which comprises passing a nitrogen-containing feed gas in contact with a first catalyst (cathodic electrode) deposited on a first surface of a proton conducting solid electrolyte and passing a hydrogen-containing gas such as diatomic hydrogen (H_2), water (steam) or any hydrogen-containing compound in contact with a second catalyst (anodic electrode) deposited on a second surface of said solid electrolyte, said first catalyst being capable of promoting the hydrogenation of nitrogen to ammonia, said second catalyst being capable of dissociating hydrogen gas to form protons (H^+) to contact said nitrogen to form ammonia and applying a voltage between said first and second catalysts through said solid electrolyte.
2. The process of claim 1, wherein said solid electrolyte comprises strontia, ceria and ytterbia ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$).
3. The process of any one of claims 1 and 2, wherein said first catalyst (cathodic electrode) comprises palladium-containing metal composition.

5

EP 0 972 855 A1

6

4. The process of any one of claims 1 and 2, wherein said second catalyst (anodic electrode) comprises a palladium-containing metal composition.
5. The process of claim 1, wherein said solid electrolyte comprises any material exhibiting protonic conductivity in the solid state. 5
6. The process of claim 5, wherein said first catalyst (cathodic electrode) comprises of palladium-containing metal composition. 10
7. The process of claim 5, wherein said second catalyst (anodic electrode) comprises of palladium-containing metal composition. 15
8. The process of claims 1, 3 and 6, wherein said first catalyst (cathodic electrode) comprises an iron-containing, platinum-containing, ruthenium-containing, cobalt-containing or any metal composition that effectively catalyses ammonia synthesis. 20
9. The process of claims 1 and 5, wherein both said first and second surfaces of the solid electrolyte are exposed to the same gaseous mixture that contains both said nitrogen-containing and hydrogen-containing gases. 25
10. The process of claims 1 or 9 wherein instead of a nitrogen-containing, a carbon and oxygen-containing compound is passing over the said first surface of claim 1 or both surfaces of claim 9 and wherein methanol is produced instead of ammonia. 30

35

40

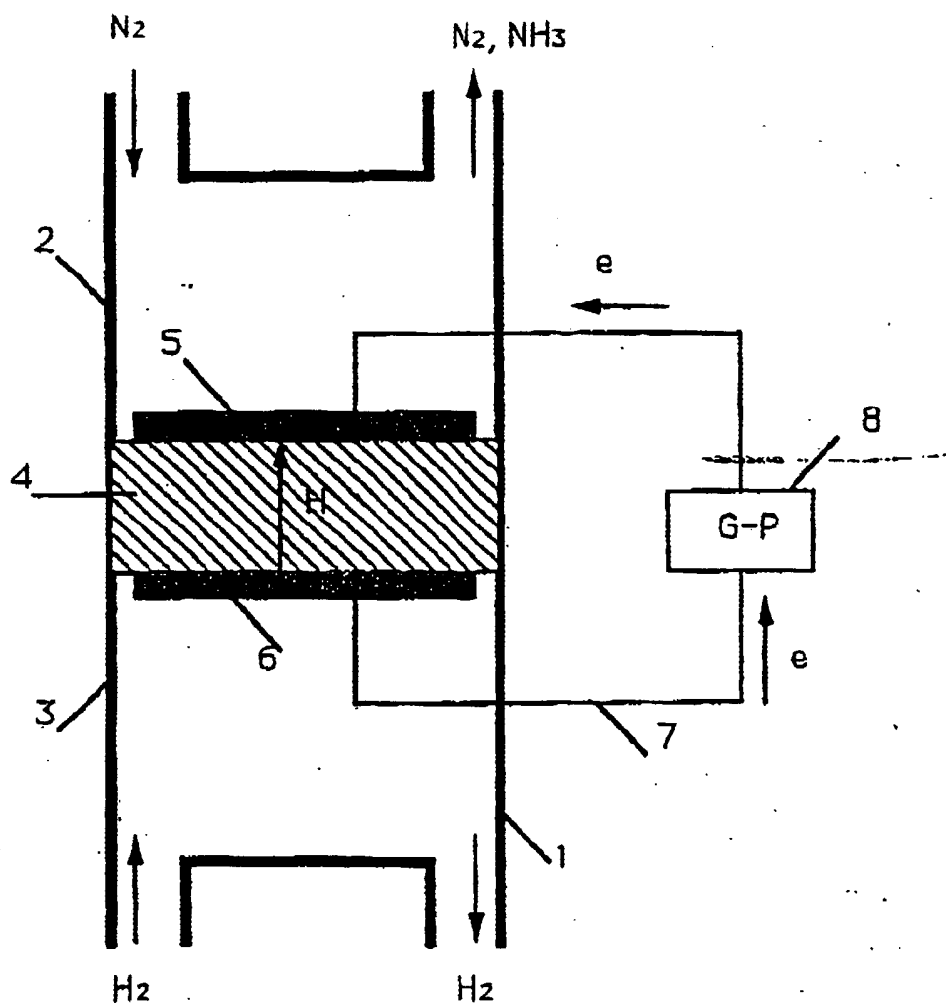
45

50

55

4

EP 0 972 855 A1

**Figure 1**

EP 0 972 855 A1

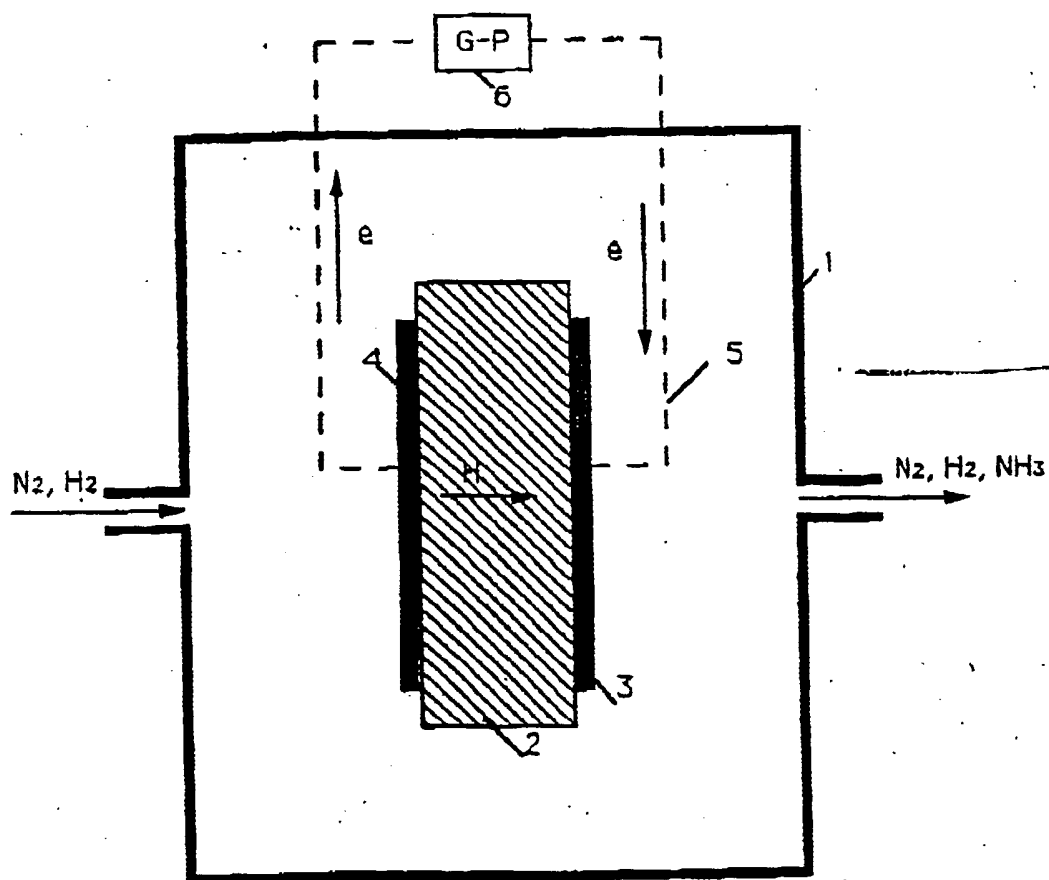


Figure 2

EP 0 972 855 A1

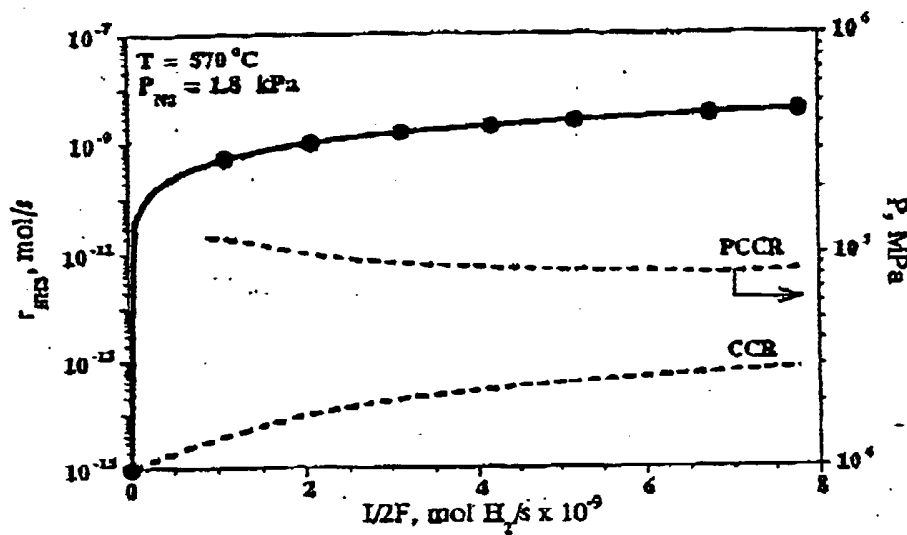


Figure 3

EP 0 972 855 A1

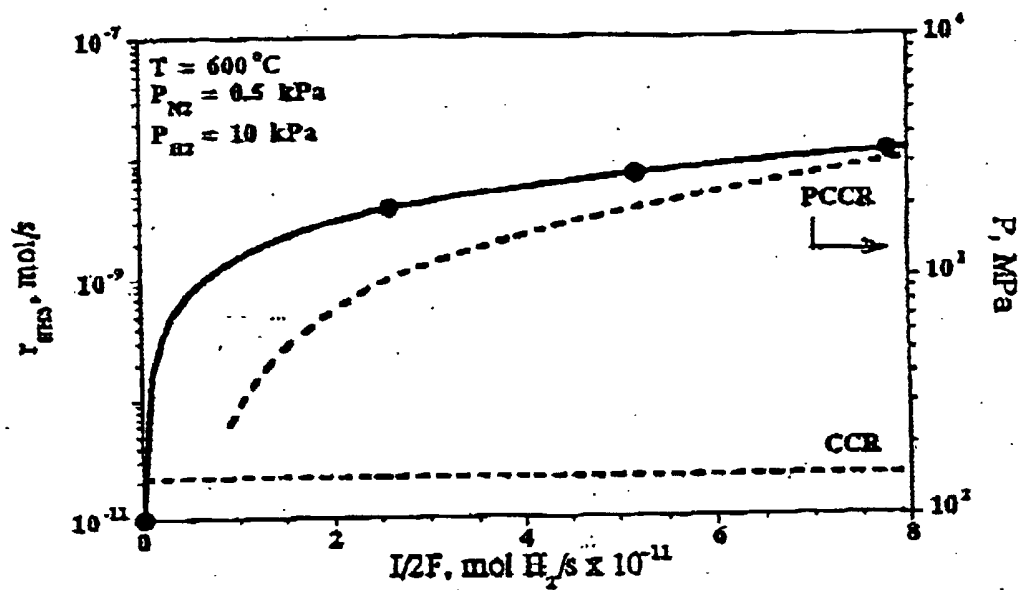


Figure 4

EP 0 972 855 A1

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 60 0008

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 001, 31 January 1997 (1997-01-31) & JP 08 246177 A (AGENCY OF IND SCIENCE &TECHNOL), 24 September 1996 (1996-09-24) * abstract *	1,5,8,10	C25B1/00
X	EP 0 480 116 A (VAYENAS C.) 15 April 1992 (1992-04-15) * column 3, line 31 - column 4, line 40 * * column 6, line 1 - line 17 *	1,5,10	
X	CHEMICAL ABSTRACTS, vol. 124, no. 26, 24 June 1996 (1996-06-24) Columbus, Ohio, US; abstract no. 347240, PANAGOS, E. ET AL: "Modeling of equilibrium limited hydrogenation reactions carried out in H+ conducting solid oxide membrane reactors" XP002091039 * abstract * & CHEM. ENG. SCI. (1996), 51(11), 3175-3180 CODEN: CESCAC; ISSN: 0009-2509, 1996,	1,5,10	
A	DATABASE WPI Section Ch, Week 8803 Derwent Publications Ltd., London, GB; Class E36, AN 88-017141 XP002091040 & JP 62 278287 A (MITSUBISHI HEAVY IND CO LTD), 3 December 1987 (1987-12-03) * abstract *	2	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		26 October 1999	Grosellier, P
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: prior art document		T: theory or principle underlying the invention E: earlier patent documents, but published on, or after the filing date D: documents cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	

EP FORM 153 (01-99) (EN)

EP 0 972 855 A1

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 99 60 0008

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on the European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-10-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 08246177 A	24-09-1996	JP 2700052 B	19-01-1998
EP 480116 A	15-04-1992	DE 69027929 D	29-08-1996
		DE 69027929 T	06-03-1997
		DK 480116 T	25-11-1996
		ES 2091812 T	16-11-1996
		GR 3021435 T	31-01-1997
JP 62278287 A	03-12-1987	NONE	

EPO FORM P-419

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82